

Ab-initio simulation of high-temperature liquid selenium

F. Kirchhoff, M. J. Gillan and J. M. Holender

Physics Department, Keele University

Keele, Staffordshire ST5 5BG, U.K.

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Abstract

Ab initio molecular dynamics simulation is used to investigate the structure and dynamics of liquid Se at temperatures of 870 and 1370 K. The calculated static structure factor is in excellent agreement with experimental data. The calculated radial distribution function gives a mean coordination number close to 2, but we find a significant fraction of one-fold and three-fold atoms, particularly at 1370 K, so that the chain structure is considerably disrupted. The self-diffusion coefficient has values ($\sim 1 \times 10^{-8} \text{ m s}^{-1}$) typical of liquid metals.

I. INTRODUCTION

Liquid Se is a highly unusual liquid because of the strong temperature dependence of its electrical conductivity, self-diffusion coefficient, viscosity, and other properties. In the trigonal crystal structure that is stable under ambient conditions, the Se atoms are bonded into infinite chains, with a rather weak interaction between chains. Diffraction measurements indicate two-fold coordination in the liquid, and the persistence of the chain structure in the liquid state is believed to account for the high viscosity and low diffusion coefficient at temperatures near the melting point (494 K). As the temperature is increased to over 1000 K, the viscosity drops by more than an order of magnitude [1], and the diffusion coefficient

increases by a factor of ~ 10 [2]. Nevertheless, the mean coordination number deduced from diffraction measurements remains close to 2.0 even for temperatures well above 1000 K. It seems likely that the chain structure is strongly disrupted at high temperatures, but it is difficult to be certain of this from diffraction data alone. The present paper reports *ab initio* molecular dynamics (AIMD) simulations of high-temperature ℓ -Se, which shed light on the three-dimensional structure of the liquid. In addition, we present information which is relevant to the study of liquid Se-based alloys such as Ag-Se and Ga-Se, for which we report AIMD results elsewhere in these proceedings [3,4].

In the AIMD technique, the energy of the system and the forces on the atoms are obtained from an *ab initio* determination of the electronic ground state for every instantaneous set of atomic positions. No assumptions are made about the interactions between atoms, and the technique is expected to give an accurate description of the covalent bonding present in any state of thermal equilibrium. The technique is therefore fundamentally different from the more traditional types of MD simulation based on assumed interatomic potentials. AIMD simulation has been used to study many liquid metals and semiconductors, and its accuracy and reliability are now well established. General reviews of the technique can be found in refs. [5].

II. SIMULATION METHODS

Our AIMD simulations are based on *ab initio* molecular dynamics (AIMD), using density functional theory within the local density approximation. We use a plane-wave basis to expand the valence orbitals, and the valence-core interaction is represented by a pseudopotential. At every step of the simulation, we solve the one-electron Kohn-Sham equations self-consistently. This is done by minimizing the total energy of the system using a conjugate-gradient technique [6]. At every MD step, the total energy was converged to better than 2×10^{-5} eV per atom. From the knowledge of the ground state, the forces on the atoms are calculated using the Hellmann-Feynman theorem. The forces are then used to integrate the

classical equations of motion of the ions. To handle the semi-metallic nature of the system, which we expect at the temperatures and pressures we consider here, we use Fermi-surface smearing, with the electronic occupation numbers treated as auxiliary dynamical variables [7–10].

We use *ab-initio* norm-conserving non-local pseudopotentials. The exchange and correlation energy is included *via* the local density approximation in Ceperley-Alder form [11]. The pseudopotential for Se was constructed using the standard Kerker method [12]. The *s* and *p* components of the pseudopotential were generated using the atomic configuration $4s^24p^4$, and the *d* component using the configuration $4s^24p^{2.75}3d^{0.25}$. The core radii were chosen to be 2.0, 2.0, 2.3 a.u for *s*, *p* and *d* components respectively. We use the pseudopotential in Kleinman-Bylander separable form [13] with the *p*-component treated as local; the non-local parts of the pseudopotential are treated in real space [14].

The system we simulated was composed of 69 atoms in a cubic cell with periodic boundary conditions. The wavefunctions at the Γ -point were expanded in a plane wave basis with a cut-off energy of 11 Ry. Test calculations done on crystalline selenium (*c*-Se) have shown that this cut-off is enough to reproduce the lattice parameters to within a few percent. A Fermi smearing width of 0.2 eV was used. The integration of the classical equations of motion was done by using Verlet’s algorithm, with a time step of 3 fs. The simulations have been performed at 870 K and 1370 K, at densities of 3.57×10^3 and 3.04×10^3 kg m⁻³. These densities correspond to experimental conditions under pressures of 10 and 100 bar respectively for which neutron [16] and X-ray [15] diffraction measurements on ℓ -Se have been carried out.

In order to avoid long MD runs to equilibrate the system, we generated initial configurations by performing MD simulations using a simple empirical tight-binding model [18]. Using this model, the system was equilibrated for 2.0 ps by rescaling the velocities, and then evolved microcanonically for another 3.0 ps. The resulting configuration was then used as initial configuration for the AIMD simulation. The AIMD run at each temperature had a duration of 3.0 ps, with averages taken only over the last 2.0 ps.

III. RESULTS AND DISCUSSION

In Fig. 1 we compare the structure factors $S(k)$ obtained from our simulations for $T = 873$ and 1373 K with the experimental results of neutron diffraction measurements [16] at the same conditions and X-ray diffraction measurements [17] at $T = 873$ and 1473 K. The overall agreement with the experiment is excellent at both temperatures. The positions and the intensity of the main and the second peaks, at ~ 3.6 and $\sim 5.8 \text{ \AA}^{-1}$ respectively, are well reproduced. The same applies for the shoulder around $\sim 2.3 \text{ \AA}^{-1}$ found for the lower temperature. However there is a slight disagreement with the X-ray data at higher temperature probably due to the different temperature involved in the experiment (1473K). The comparison with experiment at low k is more difficult due to the noise in the calculated $S(k)$ resulting from the small size of our system and the resulting lack of k -space resolution. This could explain the spurious pre-peak observed just above 1 \AA^{-1} at 1370 K. We see that with increasing temperature and pressure the amplitudes of the first and second peak decrease and the shoulder just above $\sim 2.3 \text{ \AA}^{-1}$ is damped out. The positions of the first and the second peak of $S(k)$ are unaffected by the increasing pressure and temperature.

The pair correlation functions for the two temperatures are displayed in Fig. 2 together with the experimental data from neutron and X-ray diffraction measurements. The overall agreement with the diffraction data is good. Our calculations show two prominent peaks for both temperature. Their positions are 2.31 and 3.64 \AA at $T = 870$ K and 2.30 and 3.72 \AA at $T = 1370$ K. These values directly give the first and second neighbor distances, r_1 and r_2 , within chains. It should be noted that there is some disagreement among the available experimental data for the first and second neighbor distances [15,16], probably due to the difficulty of deriving $g(r)$ from $S(k)$. Nevertheless, our findings are in good agreement with the more recent X-ray diffraction data [15], which for $T = 873$ K give $r_1 = 2.31$ and $r_2 = 3.65$ and for $T = 1473$ K $r_1 = 2.31$ and $r_2 = 3.64$. We note that there is some disagreement so far as the height of the peaks is concerned, but this difference is similar to that observed when experimental results are compared. The effect of temperature on $g(r)$

is mainly to decrease the magnitude and increase the width of the the main peak. We also note the appearance of a shoulder at ~ 2.75 Å and an increase of $g(r)$ at the first minimum, r_c . The area under the first peak of $g(r)$ gives the nearest-neighbor coordination number N_c . We find that for both temperatures selenium has an average coordination number slightly smaller than 2: $N_c=1.95$ at 870 K and 1.98 at 1370 K. This means that the chain structure characteristic of *c*-Se is preserved even at high temperature, in agreement with what is found experimentally [15,16]. The first-neighbor distance found in our calculation is shorter than the corresponding distance in *c*-Se (2.37 Å), whereas the second neighbor distance is larger (3.44 Å). This implies that as the interchain distance is increased due to the decreasing density, the covalent bonds within the chains contract [15].

Table I shows the distribution of first-neighbor coordination numbers found in our simulations. At both temperatures, the majority of the atoms are two-fold coordinated but with a significant proportion of one-fold coordinated atoms, thus accounting for the coordination number smaller than two. The effect of temperature is to decrease the proportion of two-fold bonded atoms. This change is clearly correlated with an increase in the number of one- and three-fold coordinated atoms. This confirms the suggestion made by many authors, that the effect of temperature is to decrease the average chain length. However, the high proportion of three-fold-coordinated atoms at the highest temperature indicates that the chains tend to branch, thus forming an interconnected network. To illustrate this point, we show in Fig. 3 and 4 ‘snap-shots’ of typical configurations at $T = 870$ and 1370 K. It is the presence of a significant number of three-fold-coordinated atoms at high temperature which is responsible for the appearance of the shoulder in the pair correlation function at 2.75 Å and the resulting increase of $g(r)$ at r_c . We point out that, compared with experimental data, our theoretical pair correlation functions are too large in the region of the first minimum, particularly for $T = 870$ K. The ratio of $g(r)$ at r_1 and r_c is linked to the exchange rate of atoms within the first coordination shell. The decrease of the ratio with increasing temperature thus implies a decrease of the average bond lifetime.

We have used the simulation to study the diffusion of the atoms, by calculating the

time-dependent mean square displacement. From the slope of this quantity, we estimate the values of the diffusion coefficients at 870 K and 1370 K to be $0.5 \times 10^{-8} \text{ m}^2\text{s}^{-1}$ and $1.5 \times 10^{-8} \text{ m}^2\text{s}^{-1}$. These values are typical of liquid metals, and an interesting question which further study is how the atoms manage to diffuse so fast in spite of the well-defined chain structure.

IV. CONCLUSIONS

We have shown that our AIMD simulations give a structure factor for high-temperature ℓ -Se that is in excellent agreement with diffraction data. Analysis of the simulated $g(r)$ gives a mean coordination number close to 2, but we find significant fractions of one-fold and three-fold coordinated atoms, particularly at 1370 K, so that the simple chain-like structure characteristic of the crystal is considerably disrupted. The self-diffusion coefficient at both temperatures is high, with values ($\sim 10^{-8} \text{ m s}^{-1}$) typical of liquid metals.

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TABLES

TABLE I. Distribution of coordination numbers N_c at T=870 K and T=1370 K. The cut-off radius r_c is taken to be the first minimum in $g(r)$, i.e. 2.75 Å and 2.85 Å for the first and the second temperature respectively. We show the average percentage of atoms with coordination N_c .

N_c	T=870 K	T=1370 K
1	11.3	18.6
2	83.7	66.9
3	4.9	13.5
4	0.1	1.0

FIGURES

FIG. 1. The total structure factor of liquid Se at 870 and 1370 K. Solid line represent the calculated $S(k)$. The full circles are experimental results from neutron scattering experiments done at 873 K and 1373 K under pressures of 10 and 100 bar, respectively [16]. The empty circles are experimental results from X-ray diffraction experiments done at 873 K and 1473 K under pressures of 16 and 120 bar, respectively [17].

FIG. 2. The radial distribution functions of liquid Se at 870 and 1370 K. Solid line represent the calculated $g(r)$ and the dotted and the dash-dotted lines are the experimental curves obtained from X-ray [17] and neutron [16] diffraction experiments, respectively.

FIG. 3. Snapshots of typical configurations of ℓ -Se at 870 K. Bonds are drawn between Se atoms with separation $< 3.0 \text{ \AA}$. Bonds to atoms in neighboring cells are represented by two-colored sticks.

FIG. 4. Snapshots of typical configurations of ℓ -Se at 1370 K. Bonds are drawn between Se atoms with separation $< 3.0 \text{ \AA}$. Bonds to atoms in neighboring cells are represented by two-colored sticks.







